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THE ELECTROCHEMISTRY OF MANGANESE PHTHALOCYANINE in NON-AQUEOUS MEDIA

BY

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The electrochemical behaviour of manganese(II) phthalocyanine in non-aqueous solvents is described. Three electron transfer couples are reported. These correspond to oxidation to manganese(III) phthalocyanine and reduction to mono- and di-anionic ligand complexes of manganese(II). The identities, including solvation, of the various species are confirmed via electronic and electron spin resonance spectroscopy, magnetism, and variable scan rate voltammetry.

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The Electrochemistry of Manganese Phthalocyanine in Non-Aqueous Media

by A.B.P.Lever*, P.C.Minor and J.P.Wilshire

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Abstract

The electrochemical behaviour of manganese(II) phthalocyanine dissolved in pyridine, dimethylsulfoxide, or dimethylacetamide is reported, in the presence of perchlorate, chloride and bromide supporting electrolye anions. Electron transfer couples representing net oxidation of manganese, and of the phthalocyanine ring, and two net reductions of the phthalocyanine ring are characterised by a range of electrochemical techniques, with emphasis on cyclic voltammetry. Heterogeneous rate constants are reported for several of these couples in the presence of perchlorate ion. All the couples show close to ideal reversible behaviour except at higher scan rates for chloride and bromide as supporting electrolyte anions, where some deviation is observed. This system does not exhibit such sensitivity to environment as was previously observed with iron phthalocyanine.

Introduction

Recent studies have clearly established the involvement of manganese in the photosynthetic production of oxygen[1]. Since the process requires several oxidising equivalents of chlorophyll, whose radical cation ultimately effects oxidation of the manganese site, the energetics of manganese redox processes are of singular importance[2]. We have therefore extended our studies of metal phthalocyanines[3,4], and those of others[5-9] to include redox potentials, products and electron transfer kinetics of PcMn(II)[4].

We report here the oxidation of PcMn(II) to PcMn(III), ligand oxidation of the latter, and two successive one electron reductions of the former. Differential pulse, and pulse polarography, cyclic voltammetry, controlled potential coulometry, electronic spectroscopy, magnetism and esr are presented to characterise the products.

Experimental

Preparation and purification of PcMn(II), solvents and supporting electrolyte have been previously described[3,4,10]. Argon gas, deoxygenated and dried, was employed to purge the solutions. Platinum, hanging mercury drop, and dropping mercury electrodes were used in conjunction with Princeton Applied Research models 173, 174A, 175 and 179, a 9002A X-Y recorder, and a Tektronix 5103N storage oscilloscope in electrochemical studies. All voltages are referred to commercial silver-silver chloride or saturated calomel electrodes fitted with Luggin capillaries. The voltages reported here are corrected to a saturated calomel electrode whose potential was monitored from time to time against the ferrocene/ferrocenium couple. Electronic spectra were recorded with a Varian Cary 14 or Perkin-Elmer-Hitachi model PE-340 uv/vis/nir micro-processor spectrometer. Magnetic measurements were obtained in solution by the Evans method11-13 using a Varian EM-360 nmr spectrometer. Esr spectra were observed with a Varian E-4 spectrometer, calibrated with DPPH as external calibrant, in frozen solution.

Results and Discussion

Four electron transfer steps lying between +1.0 and -1.9V (vs sce) were observed using continuous scan voltammetry (Fig.1). They represent two net oxidations and two net reductions of the bulk solution. This is similar to our experience with PcFe(II)3b which exhibits one oxidation and two reduction waves in the same region. Earlier authors6 who studied polarograms of electrochemically generated (PcMn)- were unable to obtain reproducible results in the region 0 - -1.4V. We did not investigate waves reported by Clack and Hush6 at potentials more cathodic than -1.9V.

The potentials of the three couples between 0 and -1.9V were obtained under a variety of solvent and electrolyte combinations by three electrode cyclic voltammetry on platinum electrodes ($E^o = (E_{p_a} + E_{p_c})/2$) and are summarised in Table 1. The values of E^o, so reported from slow speed scans, are essentially independent of scan rate except in the presence of halogen supporting electrolyte anion. The values of $E_{p_a} - E_{p_c}$ obtained at the diffusion limit (10 mV/s scan rate) were, in each case, within a few millivolts of ideality. Polarographs were obtained at this, or a lower, scan rate, for some of the electron transfer couples. Differential pulse polarograms (at 1 mV/s scan rate, modulation voltage 25mV p-p) were also recorded and $E_{3/4} - E_{1/4}$ determined. Half-wave potentials from the various methods agreed within 30mV. Values of n = 1 (± 10%) (n is the number of electrons involved in the electron transfer step) for the first and second reduction steps were confirmed by three electrode coulometry employing a platinum mesh electrode. Studies at higher scan rates gave values of E_{p_a}, E_{p_c}, i_{p_a}, i_{p_c} (anodic and cathodic peak potentials and currents respectively) which were subsequently analysed by the methods of Nicholson and Shain14. This identified deviations from reversibility arising from electron transfer kinetics or coupled chemical reactions. Internal cell resistance was compensated electronically.

First oxidation - $Pc(-2)Mn(III)S_2^{+}/Pc(-2)Mn(II)S_2$:4

As indicated by slow scan rate data and using tetraethylammonium perchlorate (TEAP) as supporting electrolyte, this couple is nearly reversible at the diffusion limit in all solvents investigated indicating little kinetic inhibition from either slow electron transfer or coupled chemical reactions. Controlled potential electrolysis at +0.1V yields a species whose electronic spectrum is characteristic of typical mononuclear manganese(III) phthalocyanine species reported by Calvin and co-workers15. On this basis we assign the first oxidation product to a Pc(-2)Mn(III) species.

The dependence of the half-wave potential upon solvent reflects an increased stabilisation of the divalent state with the stronger coordinating solvents (pyridine > DMSO > DMA = DMF) . A similar but more pronounced dependence is seen with iron phthalocyanines3. Cobalt(II) phthalocyanines however exhibit a reversed trend with the more strongly donor solvents favouring cobalt(III). The rationale for this varied behaviour has been presented.[16] The PcMn(III)/PcMn(II) redox potential also depends upon the supporting electrolyte with the trivalent state being favoured by the more strongly coordinating anions ($Cl^- > Br^- > ClO_4^-$). Evidently their coordination to manganese(III) is important. This is confirmed by their electronic spectra which show a marked dependence of the visible (Q) band near 700 nm upon counter ion.[17]

Previous studies have shown[4,15] that the solid species PcMn(III)X (where X is halogen, hydroxide, acetate etc) are high spin and probably five coordinate. In contrast the solution susceptibility of the highly soluble tetra-t-butylphthalocyanatomanganese(III) hydroxide, in pyridine, corresponds to two unpaired electrons within experimental error (2.6 BM at room temp.) implying low spin d4 manganese(III) which is a rare occurrence for macrocyclic ligands. Thus in strongly coordinating solvents, manganese(III) phthalocyanines may be six coordinate. Similarly, solutions of PcMn(II) in coordinating solvents are six coordinate and low spin as shown unequivocally by their esr spectra, typical of low spin d5, $S = 1/2$ species:[18]

$Pc(-2)Mn(II)(DMA)_2$ $g_{\parallel} = 1.86$ $g_{\perp} = 2.16$ $|A_{\parallel}| = 0.0138$ $|A_{\perp}| = 0.00484\,cm^{-1}$

$Pc(-2)Mn(II)(Py)_2$ $g_{\parallel} = 1.89$ $g_{\perp} = 2.16$ $|A_{\parallel}| = 0.0147$ $|A_{\perp}| = 0.00484\,cm^{-1}$

$Pc(-2)Mn(II)(4\text{-}EtPy)_2$ $g_{\parallel} = 1.98$ $g_{\perp} = 2.17$ $|A_{\parallel}| = 0.0147$ $|A_{\perp}| = 0.00475\,cm^{-1}$

Solutions of PcMn(II) in pyridine yielded a solution magnetic moment of

1.6 BM at room temp. confirming the esr characterisation as a low spin d5 S = 1/2 ion.

With TEAP as supporting electrolyte, Nicholson-Shain analysis[14] is consistent with previous evidence. The oxidation of PcMn(II) in pyridine, and in DMSO, is quasi-reversible with less than 5% variation in the unit value of (i_{p_c} / i_{p_a}) over the range of scan rates observed (10mV/s - 50 V/s). The function ($i_p/v^{\frac{1}{2}}$) is also constant. These observations are consistent with, but do not prove that both manganese(II) and manganese(III) species are six coordinate species. Similar behaviour would be expected if either species were five coordinate but rapid solvent exchange was taking place. Considering the solution magnetic data, however, it is likely that the oxidation product is $[Pc(-2)Mn(III)S2]^+ ClO_4^-$ (at least for S = pyridine or DMSO)[18]. Rather different behaviour is observed when the supporting electrolyte contains bromide or chloride ion. Both anodic and cathodic peak potentials shift at higher scan speeds consistent with a quasi-reversible electron transfer with transfer coefficient $\alpha < 0.5$.[19] There appears to be a small dependence of E^o upon X^-, though not as marked as was observed in the corresponding PcFe(III)/PcFe(II) electron transfer step.[3]

In most solvents, the more coordinating anions shift the potential cathodically relative to less coordinating ions, consistent with equilibria (1) and (2).

$$Pc(-2)Mn(II)S_2 \rightleftharpoons [Pc(-2)Mn(III)S_2]^+ + e^- \qquad (1)$$

$$X^- + [Pc(-2)Mn(III)S_2]^+ \rightleftharpoons Pc(-2)Mn(III)X(S) + S \quad (2)$$

These equilibria must reasonably occur, but must be kinetically very labile since even at the highest scan rates there is no evidence for a cathodic wave corresponding to reduction of the species Pc(-2)Mn(III)X(S), in contradistinction to the analogous iron system.[3]

Heterogeneous rate constants (k_s) for the reversible case with perchlorate ion as supporting electrolyte were obtained from the relationship:[19]

$$\Psi(\Delta Ep, n) = (\gamma^{\alpha} k_s / \pi a D_o)^{\frac{1}{2}} \quad (3)$$

where a = nF(scan rate)/RT, D_o is the diffusion coefficient, α the transfer coefficient. α was polarographically determined to be 0.48 and D_o was obtained from the Randles-Sevcik relationship. The results, reported in Table 2, indicate only a slight dependence of k_s upon solvent for the Pc(-2)Mn(III)/Pc(-2)Mn(II) couple (and no dependence for the reduction couples discussed below). When chloride or bromide are used as electrolyte anions, the coupled reactions (1) and (2) occur and the expression for the peak potential must contain equilibrium constant data for equ.(2). Since our data do not clearly distinguish a quasi-reversible electron transfer from an EC mechanism, we do not attempt to calculate rate constants in the presence of chloride and bromide ions.

However since a negligible deviation of ΔEp from the ideal 59 mV was observed at low scan rates with all solvent-electrolyte combinations it is probable that the k_s values do not differ significantly from those reported for the perchlorate anion solutions. Thus a strong Mn-X bond is not especially rate limiting where both PcMn(II) and PcMn(III) are six coordinate.

By comparison, when five and six coordination are possible, the conditions dictating different geometries for each oxidation state can provide a kinetic barrier for the redox process. In a study of the analogous TPPMn(III)Cl (TPP = tetraphenylporphyrin) Kadish and co-workers20 found that addition of imidazole to methylene chloride solutions yielded a six coordinate Mn(III) species and an out-of-plane five coordinate manganese(II) species. There was a three order of magnitude electron transfer rate reduction for the imidazole adduct relative to the chloride. Our results are consistent with Kadish's conclusion that metal movement with respect to the equatorial ligand, rather than axial bond breakage, is rate limiting. The effect of spin state change upon electron transfer rates in these manganese systems remains undetermined since PcMn and TPPMn are low and high spin respectively in both their +2 and +3 oxidation states.

Second oxidation - $Pc(-1)Mn(III)S_2^{++}/Pc(-2)Mn(III)S_2^{+}$

The second oxidation wave was observable only in DMF due to the sparing solubility of the parent species and relatively high solvent oxidation currents in all other media investigated. When observed in rigorously dry DMF at moderate scan rates (0.2 - 2.0 V/s) cathodic and anodic waves were seen at an average E^o of 0.870V. Although coulometric n values were within range of unity (n =1.28 ± 8% over six runs) , no stable species was obtained by controlled potential oxidation. Since the species on the electrode prior to oxidation is $Pc(-2)Mn(III)S_2$, the probable oxidation products are $Pc(-1)Mn(III)^{++}$ or $Pc(-2)Mn(IV)^{++}$ (neglecting solvent coordination). Although the latter cannot be entirely excluded, we prefer the former on the basis that the voltage separation between this couple and the first ligand reduction couple (see below) is 1.63V. This is in excellent agreement with the average voltage separation (1.56V) observed between ring oxidation and reduction in a series of main group metallophthalocyanines22 where no ambiguity exists.

First reduction - $Pc(-2)Mn(II)S_2/Pc(-3)Mn(II)S_2^-$

Earlier work by Clack and Hush6 mentions the intermittent appearance of two waves at -0.755 and -1.008V. Our studies show the former wave under all conditions, but the latter is seen only in inadequately purged solutions. The former wave shows almost no electrolyte anion dependence and a rather small solvent dependence (< .1V, see Table 1) . This comparative insensitivity to environment is a strong clue to the nature of the product, which must either involve reduction of the metal to $Pc(-2)Mn(I)^-$ or reduction of the ligand to $Pc(-3)Mn(II)^-$. Our earlier studies with the Pc(-2)Fe(III)/P(-2)Fe(II) couple3 reflect a stabilisation of low spin d6 $Pc(-2)Fe(II)S_2$ which results in a > 0.7V variation in potential for the solvents studied here. This was ascribed to back donation by the iron(II) species being enhanced by the stronger donor axial ligands. If Mn(I) , expected to be low spin d6, is produced during this reduction, a significant solvent effect for this ion, which should be an effective pi donor to Pc, is anticipated. Moreover when the electrochemical solution is saturated with carbon monoxide, no shift in potentials is seen from which we may conclude that this reduced species does not react with carbon monoxide. A manganese(I) species would be expected to react with carbon monoxide in parallel with the chemistry of the isoelectronic Fe(II) and Ru(II) phthalocyanines. The absence of a strong solvent effect and of reaction with carbon monoxide, argues forcefully for the first reduction product to involve reduction of the phthalocyanine ring.

Although no esr spectrum was observed with this species, this fact lends no support to either assignment since even-electron systems are often esr inactive. The electronic spectrum of the reduced solution, first reported by Clack and co-workers21 is more enlightening. Although the Q band absorption for Pc(-2)Mn(II) is blue shifted with respect to that of Pc(-2)Mn(III)Cl the shift (50 nm) is small and reflects greater repulsion between metal e_g(pi) and phthalocyanine e_g(pi*) orbitals in the former species. The monoanion , however, exhibits a Q band blue shift of greater than 130 nm placing it in the same spectroscopic region as other metallophthalocyanine anion radical species which have been unambiguously identified21 . Similarly the extinction coefficients for the visible region transitions are smaller, by more than an order of magnitude, than those observed for other phthalocyanine(-2) species10 . Finally the separation between the purported ligand oxidation and reduction is within the range observed with other main group and transition metallophthalocyanines22. Since the metal remains bivalent and the electrochemistry is fully reversible, we assume that two solvent molecules remain coordinated.

Second Reduction $Pc(-3)Mn(II)S_2^-/Pc(-4)Mn(II)S_2^{=}$

In this case reduction could yield $Pc(-3)Mn(I)^{=}$ or $Pc(-4)Mn(II)^{=}$, as the most probable products. The potentials for this couple (Table 1) indicate minimal solvent and electrolyte dependence arguing strongly for ligand rather than metal reduction as discussed above. Although polarographic results reflected the essential reversibility of this couple, cyclic voltammetry data were often rendered unreliable by high solvent background, especially at high scan rates. A Nicholson-Shain analysis was therefore not performed.

The electrochemically produced double reduction product has an electronic spectrum similar to that of its mono-anionic parent, in that the Q band energies are of relatively high energy and low intensity. The esr spectrum of the di-anion is similar to that observed for the di-anion of TsPcMn (TsPc = tetrasulfonated phthalocyanine) which has been previously assigned as d7 TsPc(-2)Mn(0).23 Were this characterisation correct its esr spectrum should have $g_{\parallel}$ and $g_{\perp}$ values comparable to the electronically analogous Pc(-2)Co(II) and Pc(-2)Fe(I). We would also anticipate that such a species should exhibit marked solvent dependence in both its esr spectrum and its electrochemistry because of the presence of an unpaired electron in the z2 orbital.

Indeed it is most likely to be five coordinate (low spin d7, cf Pc(-2)Fe(I)33b) . The esr spectrum of the di-anion is in fact very similar to that of the six coordinate low spin d6 Pc(-2)Mn(II) precursor. The reversibility observed in the electrochemistry of this species and the absence of any following reaction leads us to assume that the coordination number probably remains six with two coordinated solvent molecules. The species is therefore assigned as $Pc(-4)Mn(II)S_2$.

Conclusions: Within the range studied, the manganese phthalocyanine system gives rise to the species $Pc(-1)Mn(III)S_2^{++}$, $Pc(-2)Mn(III)S_2^{+}$, $Pc(-2)Mn(II)S_2$, $Pc(-3)Mn(II)S_2^{-}$ and $Pc(-4)Mn(II)S_2^{=}$, where in the case of the manganese(III) species, a solvent molecule may be displaced by an anion X. No evidence of manganese(I) was observed in distinction to the iron and cobalt series3,17 The electron transfer rates of the PcMn(II) electron transfer steps are similar in magnitude to those usually found in analogous porphyrin series24 . Unlike TPPMn(III)Cl however, the rate is not profoundly changed by either choice of anion or coordinating ligands. The Pc(-2)Mn(III)/Pc(-2)Mn(II) couple appears at a slightly more anodic potential than in the porphyrin series. Reduction of the phthalocyanine ring however, to form $Pc(-3)Mn(II)S_2^{-}$ appears 0.5 - 0.8V anodic of the corresponding porphyrin reduction25 . These trends are consistent with earlier views of the comparative electrochemistry of porphyrins and phthalocyanines3,26. This comparison illustrates the variation in coordination electronic and geometric structure accessible within the MN_4 class of compounds and its effect upon electrochemical properties.

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References

1) Cheniae,G.M.; Ann.Rev.Plant Physiol. 1970, 21, 467.

2) Godini,M.E.; Wallis,L.A.; Reichel,T.L.; Sawyer,D.T., Inorg.Chem. 1976, 15, 1535.

3) a) Lever,A.B.R.; Wilshire,J.P., Can.J.Chem. 1976, 54, 2514. b) Lever,A.B.P.; Wilshire,J.P. Inorg.Chem. 1978,17 ,1145.

4) Myers,J.F.; Canham,G.W.R.; Lever,A.B.P. Inorg.Chem. 1975,14, 461. This paper contains an introduction to the phthalocyanine nomenclature utilised here.

5) Rollman,L.T.; Iwamoto,R.T. J.Am.Chem.Soc. 1968, 90, 1455.

6) Clack,D.W.; Hush,N.S.; Woolsey,I.S. Inorg.Chim.Acta, 1976, 19, 129.

7) Wolberg,A.; Manassen,J. J.Am.Chem.Soc. 1970, 92, 2982.

8) Li,C.;Chin,C. Anal.Lett. 1975, 8, 291.

9) Kadish,K.M.; Bottomley,L.A.; Cheng,J.J. J.Am.Chem.Soc. 1978, 100, 2731.

10) Lever,A.B.P. Adv.Inorg.Chem.Radiochem. 1965, 7, 2731.

11) Evans,D.F. J.Chem.Soc. 1959, 2003.

12) Loliger,J.; Scheffold,R.; J.Chem.Educ. 1972, 49, 646.

13) Crawford,T.H.; Swanson,J. J.Chem.Educ. 1971, 48, 382.

14) Nicholson,R.S.; Shain,I. Anal.Chem. 1964, 36, 706.

15) Engelsma,G.; Yamamoto,A.; Markham,E.; Calvin,M. J.Phys.Chem. 1962, 66, 2517.

16) Lever,A.B.P.; Minor,P.C. Adv.Molecular relax.Inter.proc. 1980,18, 115.

17) Minor,P.C.; Licoccia,S.; Lever,A.B.P. to be submitted for publication.

18) The esr spectrum for a solution of Pc(-2)Mn(II) in DMA reported here, was that commonly obtained. However if extreme care is taken to ... DMA, another esr spectrum, apparently indicative of ... spin Mn(II) is observed on some occasions . It is possible therefore that the data reported here for both esr and electrochemical ..., may involve coordinated dimethylamine.

19) ...rger,A.; Rossiter,B. Editors, 'Physical Methos of Chemistry', ... John Wiley and Sons, Inc., New York, NY 1971 p.454

20) ...h,K.M.; Sweetland,M.; Cheng,J.J. Inorg.Chem. 1978, 17, 2795.

21) ...,D.J.; Yandle,J.R. Inorg.Chem. 1972, 11, 1738.

22) ...,A.B.P.; Minor,P.C. submitted to Inorg.Chem. Jan 1981.

23) ...on,D.J.; Smith,T.D.; Boas,J.F.; Hicks,P.R.; Pilbrow, J.R. J.Chem.Soc. Dalton, 1977, 211.

24) ...ish,K.M.; Davis,D.G. Anal.N.Y.Acad.Sci. 1973, 206, 495.

25) ...er,L.J.; Garber,K. Inorg.Chem., 1970, 9, 2644.

26) L...er,A.B.P. First Chemical Congress of the North American Continent, Mexico City, 1975, Abs. No. Inor.028.

...neous Rate Constants k_s (cm/s)

	...)Mn(III)/Pc(-2)Mn(II)	Pc(-2)Mn(II)/Pc(-3)Mn(II)
[illegible]	2.9 x 10-3	6.8 x 10-3
[illegible]	5.6 x 10-3	6.7 x 10-3
[illegible]	6.8 x 10-3	7.1 x 10-3

TABLE 1

[illegible] PHTHALOCYANINE MANGANESE[illegible][a]

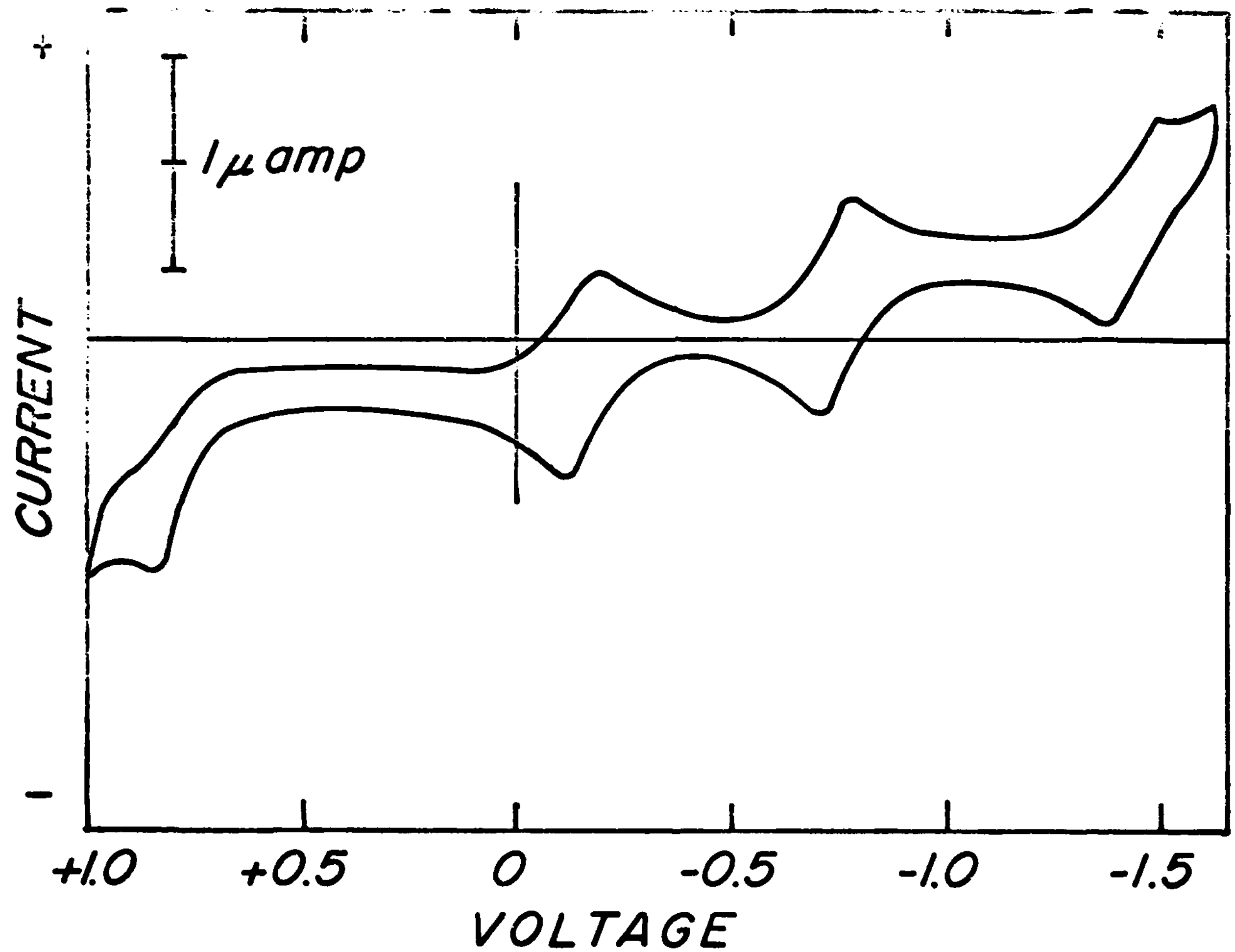
SOLVENT	SUPPORTING ELECTROLYTE	REDOX COUPLE	E^o (V)	REDOX COUPLE	E^o (V)	REDOX COUPLE	E^o (V)
PYRIDINE	TEAP	Pc(-2)Mn(III)/ Pc(-2)Mn(II)	.005	Pc(-2)Mn(II)/ Pc(-3)Mn(II)	-.785	Pc(-3)Mn(II)/ Pc(-4)Mn(II)	-1.52
	TEABr	"	-.035	"	-.710	"	-1.52
	TEACl	"	-.105	"	-.800	"	
	LiCl				-.800		-1.49
DMSO	TEAP	"	-.080	"	-.755	"	-1.39
	TEABr	"	-.085	"	-.700	"	-1.41
	TEACl	"	-.125	"	-.765	"	(-1.47)
	LiCl	"	-.125	"	-.815	"	-1.41
DMF	TEAP	"	-.140	"	-.690	"	-1.46
	TEABr	"	-.115	"	-.780	"	-1.48
	TEACl						
	LiCl	"	-.155	"	-.800		-1.50
DMA	TEAP	"	-.110	"	-.740	"	-1.34
	TEABr	"	-.130	"	-.800	"	-1.52
	TEACl						
	LiCl	"	-.140	"	-.800		

a) Average of anodic and cathodic peak voltages quoted to nearest 5 mV. All data obtained by cyclic voltammetry

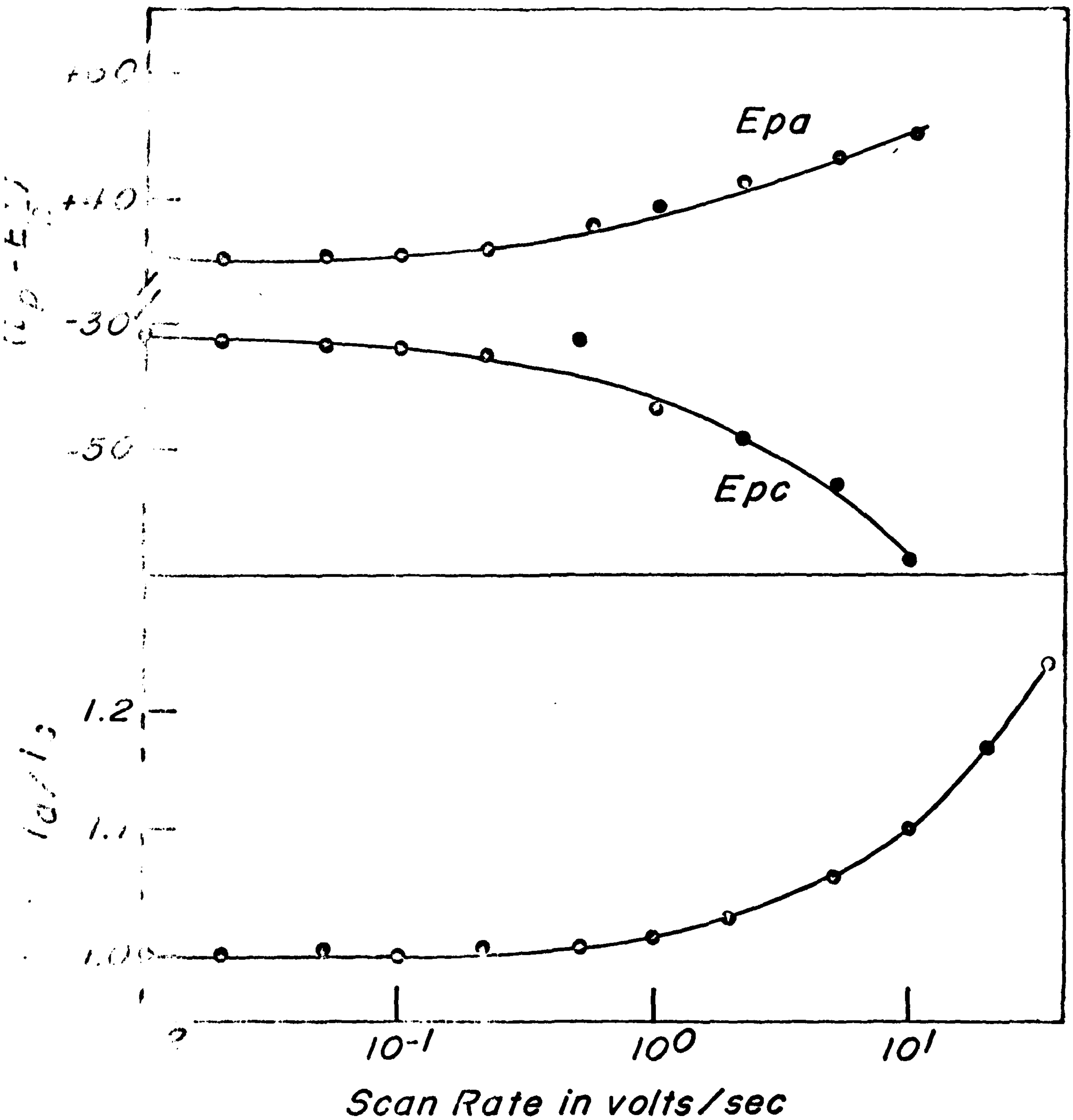
Figure legends

Fig.1 Cyclic voltammogram of PcMn(II) dissolved in dimethylformamide containing Tetraethylammonium perchlorate as supporting electrolyte. The scan rate is 50 mV/s.

Fig.2 Nicholson-Shain analytical plots for the (Py)ClMn(III)Pc(-2) / $(Py)_2$Mn(II)Pc(-2) couple in pyridine containing lithium chloride as supporting electrolyte.



+
1 μ amp
CURRENT
-
+1.0
+0.5
0
-0.5
-1.0
-1.5
VOLTAGE


Epa
Epc
$(E_p - E_{1/2})$
+30
+10
-30
-50
i_a/i_c
1.2
1.1
1.00
10^{-1}
10^{0}
10^{1}
Scan Rate in volts/sec